Albert.J.Boettler@usa.dupont.com

09/01/00 01:00 PM

To: Andy Park/R2/USEPA/US@EPA

cc: Barry Tornick/R2/USEPA/US@EPA, FFaranca@dep.state.nj.us, Kevin.P.Garon@usa.dupont.com

Subject: GW-SW interaction response to Region 3 comments and Revised draft guidance

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Andy,

I need to correct my statement in my previous message. We are actually >10X for some of our constituents in monitoring wells but the constituent concentrations based on the modeling are well below the ambient water quality prior to discharging into surface water. Thus, our modelling demonstration comes under step 6 rather than 5 as I indicated in my earlier statement.

If you have any problem opening the word document in my earlier message, let me know and we will send you a hard copy.

Give me a call to further discuss.

Al

Albert.J.Boettler@usa.dupont.com

08/31/00 06:23 PM

To: Andy Park/R2/USEPA/US@EPA

cc: Barry Tornick/R2/USEPA/US@EPA, FFaranca@dep.state.nj.us

Subject: GW-SW interaction response to Region 3 comments and Revised draft guidance

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Andy,

I don't know where the disconnect is, but our Region II approach at Chambers Works is clearly consistent with our approach in Region III. At Chambers Works there are enough data to indicate that the total groundwater constituent loading to the river is very, very minor compared with the permitted outfall. Also, even more important is the modeling shows that the mixing in the aquifer as a result of the tidal action is adequate to bring the concentration of the constituents well below the ambient water quality standard before it actually discharges to the river. Because we are not above 10 times appropriate criterion i.e. Step 5, we don't need to go to Step 6 of the determination. The recent groundwater/surface water work with Region III focuses on Step 6.

Call me to further discuss. I've included the latest version of the document being worked on with Region III.

(See attached file: GW_SW_ rev 5_July700.doc)

Al

-------------------- Forwarded by Kevin P Garon/CL/DuPont on 08/28/2000 02:55 PM ---------------------------

Park.Andy@epamail.epa.gov on 08/28/2000 11:43:34 AM

To: Tornick.Barry@epamail.epa.gov
cc: FFaranca@DEP.state.nj.us, Kevin P Garon/CL/DuPont,
Basso.Ray@epamail.epa.gov, Goldblum.Deborah@epamail.epa.gov
Subject: Re: Effect on GW concentration due to tidal fluctuations

I also understand that an issue of potential ecological risks/impacts is being
addressed by DuPont in conjunction with Region 3 but is not part of DuPont's
proposal to Region 2. Just as we expect that EPA will speak with one voice on
the EI-related GW-SW issue, the main ideas of DuPont's proposal ought to be
consistent throughout, not tailored to Region-specific comments and
concerns.
It appears that, in order to achieve that, any DuPont's proposal addressing the

EI-related GW-SW issue must address not only the groundwater concentrations influenced by tidal fluctuations, if any, but also potential ecological risks/impacts.

- GW_SW_ rev 5_July700.doc

4 DETAILED CA750 EI - ASSESSMENT OF SURFACE WATER AND SEDIMENT IMPACTS (Step 6)

Introduction

This section is intended to provide a much more detailed discussion of Step 6 in the EPA worksheet for the CA750 EI, migration of contaminated groundwater under control, for cases where "contaminated" groundwater is discharging to a surface water body. Please note that the user should be familiar with the overall process for the CA750 EI, as explained in Section 3, before proceeding through the detailed discussion provided here.

An element of the CA750 EI is the potential impacts of <u>current</u> groundwater discharges to surface water on the surface water environment (surface water and sediment ecosystems). However, groundwater-surface water interactions are complex, as is contamination of those media. There are, typically, many sources of contaminant loading to surface water and sediments, both historical and current. Furthermore, it is often difficult to distinguish current groundwater impacts (those relevant to the EI determination) to surface water and sediments from other sources, past and present (which are not subjects of an EI determination). Equally complex is the evaluation of the ecological significance of surface water and sediment contamination, as there can be many stressors affecting ecological receptor populations, including man-made and natural media quality, temperature, salinity, sediment type, etc.

This section is intended to help guide, in more detail, evaluations of potential impacts of current groundwater discharges on surface water bodies. It includes methods to:

- evaluate existing and readily available data,
- determine whether sampling is appropriate and to guide sampling approaches, and
- evaluate any sampling data.

The basis of the guidance is a weight-of-evidence approach which acknowledges that although no single factor is likely to be a determinant, a preponderance of evidence can establish the significance (or lack thereof) of groundwater impacts on surface water and sediment quality. A tiered approach is presented that begins with the use of available information about the groundwater environment, potential contaminants of concern (COCs), and the receiving water body ecosystem and provides a logical "stepwise" process leading to decisions regarding potential impacts, sampling and data evaluation. The guidance provides summary charts that describes the evaluation steps and a set of examples to illustrate the process. A summary table detailing factors to be considered and their potential relevance at sites is included for reference.

The evaluations in this guidance should be performed prior to determinations regarding sampling. This guidance is intended to assist in determining if sampling is needed and, where needed, to focus and guide sampling and data evaluation efforts. Evaluators are encouraged to use methods suggested in the guidance to identify data needs, develop data quality objectives and establish data evaluation procedures prior to any sampling.

The emphasis in CA750 is on actual, current discharges and their effects. This document lays out a method to evaluate those effects based on a weight-of-evidence approach, and is intended to facilitate CA750 evaluations. However, as noted earlier, groundwater/surface water/sediment dynamics and ecological dynamics are complex technical areas. It is recommended that technical specialists in relevant areas (e.g. hydrogeology, surface water hydrology, environmental chemistry, and ecological risk assessment) be consulted as appropriate.

Overview of the Evaluation Process

The Environmental Indicator "Migration of Contaminated Groundwater Under Control" (CA750) has two elements, both of which apply to "contaminated" groundwater (i.e., groundwater containing constituents above an appropriate level of concern), as described below.

- When contaminated groundwater is not discharging into surface water, the EI goal is no migration of contaminated groundwater beyond its current spatial limits (lateral and vertical level of concern), and the presence of monitoring wells located proximate to the outer perimeter to the plume confirm no migration over time. EPA's guidance suggests that "limited" migration to facilitate natural attenuation can be acceptable; but in such cases natural attenuation should be part of a formal remedy decision including public participation (see EPA CA750 guidance, page 11, footnote 2).

- When groundwater is currently discharging to surface water, the EI goal is no surface water or sediment impacts (from the current discharge) that have the potential to result in unacceptable human health or ecological impacts.

Step 6 of EPA's CA750 process (see Attachment 1) addresses the case where groundwater discharges into surface water (above 10 times an appropriate criterion, i.e., Step 5 evaluation). A determination is made as to whether the discharge of constituents of concern (COCs) in "contaminated" groundwater into surface water can be <u>shown</u> to be "currently acceptable". The discharge is defined as " currently acceptable" if it does not cause "significant" impacts to surface water, sediments or ecosystems. This guidance addresses this aspect of the CA750 determination.

EPA's CA750 EI worksheet lists some factors that should be considered in performing an EI or interim assessment. Factors that contribute to the assessment of the impact of discharging contaminated groundwater include:

- Properties of the groundwater environment, e.g., nature and rate of groundwater flow.
- Factors that influence rates of groundwater discharge to surface water features (e.g. tidal effects, sediment type in discharge zone).
- Which groundwater constituents should be considered constituents of concern (COCs)?
- Contaminant concentrations for COC in groundwater.
- Factors that affect contaminant discharge mass and concentration (e.g. biological and physiochemical attenuation effects in the discharge zone).
- Properties of the surface water body, (e.g., size, flow rate).
- Properties of the sediment (e.g., nature of the sediment (sand, silt, clay), organic carbon content).
- Receptor characteristics (e.g., use, classification, habitats, and contaminant sensitivities).
- Physical, chemical and eco-toxicological properties of the COCs.
- Other current and historical sources of surface water and sediment contamination.
- Comparison of surface water and sediment sample results to available and appropriate surface water and sediment criteria.
- Observed effects on receptors (such as from bioassays, benthic surveys or other site-specific ecological evaluation).

Use of these factors may vary from simple mass input calculations (to determine the potential to exceed relevant criteria) to complex site-specific evaluations of very specific effects. The intent of this guidance is to help evaluators choose the appropriate level of detail in the analysis needed to make an EI determination. Impacts to surface water and sediments are described separately (but not exclusively) in the following discussion.

As stated earlier, one of the main goals of this document is to develop a logical, stepwise process using a weight-of-evidence approach in determining if and when sampling of surface water and sediments is needed. It is important to note that in this approach, not all evidence is weighed equally, even in a qualitative analysis. For instance, if a particular route of exposure is through inhalation, and a COC is non-volatile (assume no particulate transport) and bioaccumulative, the fact that the COC is non-volatile should carry much more weight than the fact that the chemical bioaccumulates. This is important because there are several decision points in the following process where evaluation of a specific factor or type of evidence may provide sufficient proof to eliminate the COC from further analysis.

EI Data Evaluation of Surface Water & Sediments Impacts – Overview

Evaluation for Surface Water

1. **Determine COCs based on relevant criteria & environmental fate**

- Initial screen against NAWQC or MCL, as appropriate
- Review potential for COC to volatilize, sorb, or degrade. Consider screening out materials that are highly volatile ($H > 10^{-3}$ atm-m^3/mol), highly sorptive ($\log K_{oc} > 3$) or highly degradable (half-life <5days) from SW evaluation
- Determine if COCs have penetrated sediments into the biologically active zone and is present in the water
- Retain COCs that strongly bioaccumulate and/or those that may have penetrated the sediments

2. **Determine mass flux of relevant COCs**

- For initial evaluations use: groundwater flux x average concentration
- Use average concentration in discharging plume
- Factor in attenuation in discharge zone (biological, sorption, etc.), as appropriate
- For initial estimates of groundwater flux use $Q = KiA$

3. **Estimate surface water concentration**

- Initial evaluations use mass flux/surface water flow
- 7Q10 for acute effects
- Harmonic mean for chronic effects
- Consider effects of tidal variations (model)

4. **Compare estimated concentration to relevant criteria; Determine potential significance**

- Examples of "criteria" include:
  - NAWQC; MCLs (if drinking water source); FDA fish advisories levels (if appropriate); State Water Quality Criteria; NPDES Limits
- Develop "criteria" from ecological toxicity values (e.g., LC_{50}; EC_{50})
- Determine significance based on potential human/eco-toxicity at these concentrations taking mitigating factors

5. **Evaluate estimated concentration against background**

- Evaluate background likely from other sources
  - Current upstream/downstream point sources
  - Current upstream/downstream non-point sources
  - Historical use and impact
- Evaluate whether effects of groundwater discharge can be differentiated from background
- Evaluate whether effects of groundwater discharge are significant vs. background

DRAFT

6. **EI Determination for Surface Water Impacts – <u>Weigh all of the evidence</u>**

- If estimated surface water concentration from current groundwater discharge < screening levels, can determine "YE"
- If estimated SW concentrations resulting from GW discharge> screening levels but are < background and cannot be discerned from background contributions, can determine "YE"
- If estimated SW concentrations resulting from GW discharge > screening levels but are < background and can be discerned from background contributions, can determine either "YE" if not significant or "IN" <u>if potentially significant</u>.
- If estimated surface water concentration from current groundwater discharge > screening levels and > background can determine "IN" and develop a plan to determine significance, or "NO" if enough data exists to determine that the discharge is significant.

More detailed site specific data regarding current groundwater and other discharges can be collected as necessary to refine the screening evaluation

<u>Evaluation for Sediments</u>

1. **Determine COCs based on environmental fate of potentially eco-toxic COCs**

- Consider all COCs
- Screen initially against sediment guidelines, as appropriate to ecosystem
- Review COCs for eco-toxicity. Consider screening out low eco-tox materials (e.g, LC_{50} *(96 hr fish; 48 hr daphids)* >100 ppm), taking into account potential accumulation
- Consider screening out constituents that do not sorb, and that are volatile, and degrade (see surface water step 1).

2. **Evaluate propensity to accumulate or migrate**

- Generally, COCs with $K_d > 10$ are considered immobile (tend to accumulate) and those with $K_d < 1$ are mobile (do not tend to accumulate)
- COCs with log 10 K_{oc} or $K_{ow} < 3$ are considered non-accumulative
- Sediments with organic fraction carbon < 0.2% are typically non-accumulative
- Consider screening out constituents that do not accumulate
- Determine if COCs have penetrated sediments into the biologically active zone
- Retain constituents that potentially accumulate and/or those that may have penetrated the sediments

3. **Evaluate the sensitivity of receptors/habitats**

- Habitat, e.g., manmade or natural; pristine or industrial
- Receptor type, e.g., threatened /endangered
- Other eco-stressors, e.g., food sources, water temperature, sediment type

4. **Compare estimated concentration to relevant criteria; Determine potential significance**

- Based on propensity to accumulate, compare estimated sediment concentrations to relevant criteria for appropriate eco-systems
- Sediment criteria/guidelines, eco-tox criteria
- Determine significance based on eco-toxicity, bioaccumulation, receptors/habitats & mitigating factors

5. **Evaluate potential impacts versus background**

- Evaluate background likely from other sources
  - Current upstream/downstream point sources
  - Current upstream/downstream non-point sources
  - Historical use and impact
- Evaluate whether effects of groundwater discharge can be differentiated from background
- Evaluate whether effects of groundwater discharge are significant vs. background

6.

EI Determination for Sediments Impacts – Weigh all of the evidence

- If no eco-toxic constituents in current groundwater discharge expected to accumulate in sediments can determine "YE"
- If eco-toxic constituents in current groundwater discharge expected to accumulate in sediments in concentrations > relevant levels but < background and cannot be discerned from background, can determine "YE"
- If eco-toxic constituents in current groundwater discharge expected to accumulate in sediments in concentrations > relevant levels but < background and can be discerned from background, can determine either "YE" if not significant or "IN" if potentially significant.
- If eco-toxic constituents in current groundwater discharge expected to accumulate in sediments in concentrations > relevant levels and > background, can determine "IN" and develop a plan to determine significance, or "NO" if enough data exists to determine that the discharge is significant.

More detailed site specific data regarding current groundwater and other discharges and sediment quality can be collected as necessary to refine the screening evaluation.

Detailed Data Evaluation Steps for Surface Water

The following evaluation steps are intended to help guide evaluation of potential impacts of current groundwater discharges on surface water quality. They present a step-wise, weight-of-evidence approach to focus on constituents of concern and evaluate potential surface water quality impacts of current groundwater discharges using existing or readily available information for most sites.

1. Determine which constituents in the discharging groundwater are COCs that should be carried forward for further evaluation based on their physiochemical properties.
   - Consider screening out constituents whose average discharge concentrations are below relevant surface water comparison criteria (e.g., Ambient Water Quality Criteria, MCLs for drinking water supplies). Due to mixing that occurs in surface water and the mobility of surface water receptors, average discharge concentrations should generally be considered unless specific characteristics of the receiving water suggest otherwise. The weighting of this factor should be based on the quality of the data.
   - The environmental fate of the constituents should be considered, particularly Henry's Law constant (measure of a COCs propensity to partition from water to air) and the propensity of the constituent to sorb to sediment, to evaluate whether the constituent is likely to be present in surface water (vs. air or sediment). Constituents that are not likely to be present or to persist in surface water can be significantly weighted and considered for potentially screening out from further evaluation for surface water impacts, though a similar evaluation for their potential sediment impacts should be made. These evaluations should be made based on readily available data (e.g. published or typical values). These parameters may also be estimated using spreadsheet models, e.g., the fugacity model developed by Utah State University and accessible at www.engineering.usu.edu/uwrl/www/faculty/fugacity/fugacity.html. These include:
     - Henry's Law constant (H) is an indication of the propensity of a chemical to volatilize from the aqueous state. If H < 10^{-7} atm-m^3/mol, the constituent will not volatilize rapidly and would be expected to remain in water. If H > 10^{-3} atm-m^3/mol, the constituent will tend to rapidly volatilize from the aqueous state and would not be expected to persist in the water (Montgomery, 1996; Dragun,1988).
     - The propensity for constituents to preferentially partition to sediments can be evaluated based upon partitioning coefficients, including their soil/water partition coefficient (K_d), octanol-water partitioning coefficient (K_{ow}), organic carbon-water partitioning coefficient (K_{oc}) and the fraction of organic carbon in the sediments (f_{oc}).
     - For organics, $K_d = K_{oc} \times f_{oc}$. In general, compounds with K_d >10 are considered immobile, and will, typically, sorb to sediment and would not be expected to persist in surface water. If K_d < 1, the constituent is generally mobile in water and would not be expected to sorb to sediment (Montgomery, 1996; Dragun,1988).
     - The nature of sediments in the discharge zone is important for determining the likelihood of a constituent accumulating in sediments. Primarily granular sediments or sediments with f_{oc} of less than 0.2% (DiToro *et al,* 1991) are generally not considered to accumulate constituents while finer and more organic sediments are more likely to accumulate constituents. Typical values of f_{oc} for common sediments are available in the literature. However, constituents having a large K_{oc} may still appreciably sorb to sediments with low organic content, and therefore, K_d should be used to assess the tendency for a COC to accumulate in sediments.

Low conc.?? high likely

Concentration dependency?!

How about in between?

- Constituents with log10 K_{oc} or log10 K_{ow} less than 3 are generally considered not likely to accumulate in sediments and would be expected to enter the water column where they may or may not volatilize to the atmosphere depending upon their Henry's Law constant.
- Where more detailed evaluations of sediment metal accumulation and potential bioavailability are warranted, the acid volatile sulfide-simultaneously extracted metal (AVS-SEM) approach can provide a measure of bioavailability for Cd, Cu, Pb, Ni, Zn and Ag. The approach is not currently applicable to other metals. While AVS-SEM approach may not always be predictive of the presence of toxicity due to these metals, it is generally predictive of the lack of toxicity due to these metals. In addition, the AVS content of sediments may be used to evaluate the mobility of metals within sediments. Other factors that influence form and fate of metals in the environment, such as pH, temperature and Kd, should also be taken into account.
- Other mechanisms that may affect the fate of constituents in the discharge zone or surface water environment are biodegradation (biological attenuation), hydrolysis (reaction with water) and photodegradation (reaction with light). Information on these qualities of a constituent can often be found in common reference sources. (Howard *et al*, 1991.)

- Use of a sorption criteria for screening is an attempt to account for the retardation of COC movement through the sediment. The impact of retardation will vary depending on characteristics of the sediment such as depth and organic carbon content. In some cases, COCs with log K_{OC} values less than 3 will be retarded such that they have not reached the biologically active surface layer of the sediment or the water column, which could seem contrary to the discussion above. Therefore, estimation of whether or not penetration of sediments has occurred is important as a screening criterion. If the COC has not penetrated the sediment, one can stop the investigation of surface water impacts from groundwater discharge. A proposed method for evaluating breakthrough is discussed in Appendix 1.

These evaluations should be used to develop enough evidence to determine if COCs can be screened out so as to focus further evaluation on those constituents of potential concern.

2. Once COCs have been determined an estimate should be made of COC mass flux to the surface water body. Generally this involves a simple combination of the groundwater mass flux and average plume concentrations at the point of discharge with consideration of any significant attenuation mechanisms. Again, if warranted more detailed evaluations can be performed via sensitivity analysis and/or computer calculations and simulations (modeling) if sufficient data exists.
   - Average concentration of COCs in the discharging plume at the point of discharge should be determined by weight averaging concentrations over the plume at the plume discharge area (assuming that there is enough data). If it is agreed that there are not enough data to determine flux accurately, the next phase of the RFI can be focused to collect the required information. In addition, sensitivity analyses and watershed mass balance approaches can be performed to determine the sensitivity of the analysis to these parameters.
     - Where COC attenuation mechanisms are expected to be significant (e.g. biological attenuation in the discharge zone) they should be factored into the mass flux estimate.
   - In estimating groundwater volumetric flux to the surface water body, first evaluations should be based upon Darcy's equation ($Q=KiA$) where K= hydraulic conductivity, A is the discharge area (cross section of the contaminant plume at the discharge point) and i = the hydraulic gradient at the point of discharge. If necessary, more detailed evaluations can be made through sensitivity analysis and/or computer modeling.
     - Hydraulic factors that can affect groundwater volumetric and/or COC mass flux, such as tidal variations in the receiving water, should also be considered. In tidal receiving waters groundwater discharge varies with tidal cycle. Tidal fluctuations have an effect of flushing the aquifer, thereby reducing concentrations entering the surface water body as compared to similar conditions in a non-

tidally influenced system (Yim and Moshen, 1992). However, this enhanced mixing associated with near-shore tidal action (termed "tidal pumping") may cause the COC to break through into the surface water system earlier than in a non-tidal system. The degree of mixing is a function of the amplitude and period of the tides and the aquifer storativity and hydraulic conductivity (Johnston, 1998) and should therefore be examined on a site-specific basis.

3. The resulting effect of COC mass flux on surface water concentrations should be evaluated. This involves calculating concentrations resulting after mixing with the surface water. In general, unless specific aspects of the surface water body suggest otherwise, the contaminant mass flux should be calculated to mix with a readily available flow estimate within a calculated mixing zone for the water body. Mixing zones should be approximated on a site-specific basis. In our experience, we have at some sites justified using the entire width of a surface water body, while at other sites used only 1/500th of the fresh water flow in a surface water body. A site-specific approach is recommended when determining the use and size of a mixing zone.

   - Appropriate surface water flow rates are generally available from US Geological Survey gaging stations.
     - For acute effects (both ecological and, if appropriate, human water use) the appropriate flow estimate is generally the 7Q10 value, an estimated 7 day low flow period anticipated to occur in a 10 year period.
     - For chronic effects (such as carcinogenic effects) a long-term average flow represented by the harmonic mean is most appropriate.
   - Tidal effects in a surface water body should be taken into account where they occur. Tidal fluctuations can result in significant attenuation of COCs in the bank storage area. Tidal effects in surface water can be accounted for by adding a dispersion term to the calculation of water column concentrations through application of a simple mixing model. However, effects on subsurface chemical processes should also be considered for tidal water bodies. Because the chemical makeup of seawater differs from groundwater (e.g., ionic strength, concentrations of dissolved organic matter (DOM) and colloidal matter, redox potential, pH, and buffering capacity are higher), chemical fate processes of a COC in groundwater may be affected. Processes that may potentially be affected include chemical equilibrium and partitioning, complexation and precipitation (especially for metals), and reaction kinetics.

4. Next, the estimated surface water COC concentrations attributable to groundwater discharges should be compared to relevant surface water screening levels to evaluate their potential significance, which should be viewed in light of background water quality.
   - There are various sources of appropriate screening values
     - EPA's National Ambient Water Quality Criteria (NAWQC)
     - Maximum Contaminant Levels (MCLs), where the surface water is a drinking water source
     - Food and Drug Administration (FDA) Fish Advisory Levels (where these exist for bioaccumulative materials)
     - State ambient water quality criteria
     - Water quality-based effluent limits (WQBELs) in a facility's NPDES permit
     - Toxicological values (e.g., derived from EC50, LC50).

5. Consider potential background sources of contaminant loading to surface water and their relative effects on surface water quality to help determine whether potential groundwater discharges are significant in light of total loadings to the receiving water. This step is meant to put the current groundwater discharge in context with other discharges both past and current. Potential loading sources include:
   - Current upstream (and, in tidal waters, downstream) point source loadings such as NPDES discharges.
   - Current upstream (and, in tidal waters, downstream) non-point source loadings such as storm water runoff, combined sewer outfalls, agricultural runoff, atmospheric deposition, etc.

- Historical use and impact to the surface water body (e.g. history of sediment contamination).

These steps should allow the project team, using existing or readily available data, to:

1. Narrow the focus of the evaluation to constituents most likely to present potential impacts.
2. Estimate COC mass flux into a surface water body.
3. Estimate COC concentrations in the surface water body.
4. Evaluate the significance of those concentrations.
5. Determine whether the surface water impact of discharging groundwater is likely to be discernible from "background" impacts and the significance relative to other discharges.

Where this initial evaluation suggests that current groundwater discharges may be causing measurable surface water impacts above background and above applicable screening criteria, consideration should be given to a more detailed evaluation.

Data Evaluation Steps for Sediments

The purpose of the following steps is to evaluate the potential impact of current groundwater discharges on the sediment ecosystem in the receiving water. It begins with a weight-of-evidence screening process to focus the evaluation by determining which constituents may be considered to be screened out from further consideration for potential concern for sediment based ecological receptors so that additional evaluations can be focused on COCs. This evaluation is intended to be performed with existing or readily available data and to guide any further evaluations or data collection. It should be noted that evaluation of the sources and significance of sediment contamination is a rapidly developing field. As with surface water, potential impacts on the sediment ecosystem need to be considered in relation to background sediment conditions and impacts.

1. Determine which constituents in the discharging groundwater are COCs that should be carried forward based on the eco-toxicity and environmental fate of constituents present in the discharging groundwater should be evaluated.

   - There are a range of aquatic/sediment ecological toxicity criteria (e.g., screening criteria, including sediment guidelines and ecological toxicity criteria) available. Examples of screening criteria include National Ambient Water Quality Criteria and Sediment Guidelines, State water quality criteria and toxicity benchmarks.
     - ➢ There are relatively few sediment quality guidelines available at this time. These values should be used with caution to ensure they are appropriate to the nature of the sediment ecosystem under consideration.
     - ➢ Constituents with relatively low eco-toxicity (based on both aquatic and sediment characterizations) can be weighed heavily to be screened out from further consideration. Where constituents are present in discharging groundwater at concentrations below relevant surface water criteria they can generally be screened out from further consideration unless specific characteristics suggest further evaluation (e.g. significant accumulation in sediment). Generally, average groundwater concentrations should be evaluated unless specific factors of the site suggest some other concentration value should be considered. A COC is considered to have low acute ecological toxicity when its 96-hr LC_{50} in a fish or 48 hour EC_{50} invertebrate bioassay is 100 mg/L or greater. It is important to review other information on low toxicity COCs for their ability to bioaccumulate or persist in the environment. Even those COCs considered to have high acute toxicity (96-hr LC_{50} or EC_{50} of 1-10 mg/L or less) may not pose a significant hazard if they also have a short half-life in the environment (short = 5 days or less) or readily biodegrade. Where reasonably representative sediment concentration data are already available and concentrations are below relevant screening criteria for certain constituents, those constituents should be considered for screening out from further evaluation.

- The environmental fate of constituents in discharging groundwater should be evaluated to determine whether the constituent is likely to present the potential for significant impacts on the sediment ecosystem.

  Environmental fate can be evaluated based on several factors (such as Henry's Law constant, biodegradation potential, tendency to hydrolyze, photodegradation potential and effects of oxidation and reduction) that are often available in common references.

  ➢ Henry's Law constant (H) is an indication of the propensity of a chemical to volatilize from the aqueous state. If $H < 10^{-7}$ atm-m^3/mol, a constituent will not tend to volatilize rapidly and may persist in the aqueous environment or accumulate in sediments. If $H > 10^{-3}$ atm-m^3/mol, the constituent will tend to rapidly volatilize from the aqueous state and is unlikely to persist in water or sediment (Montgomery, 1996; Dragun,1988).

  ➢ Other mechanisms that may affect the fate of constituents are biodegradation (biological attenuation), hydrolysis (COC reaction with water), photodegredation (reaction with light), and the affects of oxidation and reduction. The rate at which these reactions occur can sometimes be found in literature or estimated. (Howard *et al*, 1991).

  ➢ Constituents that are unlikely to persist in the sediment environment (e.g. highly volatile or highly biodegradable materials) can be considered for screening out from further evaluation.

2. The propensity of a constituent to accumulate in or migrate through sediments as well as to partition from sediments to sediment pore water, where it can become bioavailable, should be evaluated.

- The propensity of a constituent to accumulate in and migrate through sediment can be characterized by partitioning coefficients, including the soil/water partitioning coefficient (K_d), octanol-water partitioning coefficient (K_{ow}) and organic carbon-water partitioning coefficient (K_{oc}). These coefficients are available for many constituents in common references.

  ➢ For organics, $K_d = K_{oc} x$ fraction organic carbon in sediment, or f_{oc}. If $K_d > 10$, the constituent is generally immobile and will tend to sorb to sediment. If $K_d < 1$, the constituent is generally mobile in water and will tend not to sorb to sediment.

  ➢ Constituents with log10 K_{oc} or log10 K_{ow} less than 3 are generally considered not likely to accumulate in sediments.

  ➢ The nature of sediments in the discharge zone is important for determining the likelihood of a constituent accumulating in sediments. Primarily granular sediments or sediments with f_{oc} of less than 0.2% (Di Toro *et al,* 1991.) are generally not considered to accumulate constituents while finer and more organic sediments are more likely to accumulate constituents. Typical values of f_{oc} for common sediments are available in the literature. However, constituents having a large K_{oc} may still appreciably sorb to sediments with low organic content, and therefore, K_d should be used to assess the tendency for a COC to accumulate in sediments.

  ➢ Similar to *Step 1* of the surface water evaluation, an analysis should be performed to determine whether the COCs may have penetrated the sediments into the biologically active zone (Appendix 1).

  ➢ Constituents that appear unlikely to have penetrated the sediments or those that are unlikely to accumulate in sediment <u>and</u> are not expected to present significant aqueous toxicity in the sediment ecosystem should be screened out from further evaluation.

  ➢ Where more detailed evaluations of sediment metal accumulation and potential bioavailability are warranted, the acid volatile sulfide-simultaneously extracted metal (AVS-SEM) approach can provide a measure of bioavailability for Cd, Cu, Pb, Ni, Zn and Ag. The approach is not currently applicable to other metals. While AVS-SEM approach may not always be predictive of the presence of toxicity due to these metals, it is generally predictive of the lack of toxicity due to these metals. In addition, the AVS content of sediments may be used to evaluate the mobility of metals within sediments.

Other factors that influence form and fate of metals in the environment, such as pH, temperature and Kd, should also be taken into account

3. The sensitivity of potential ecological receptors/habitats in the surface water/sediment environment should be evaluated for constituents that have been determined to be COCs.
   - This should include an evaluation of the various stressors affecting that environment, both natural and manmade, and a consideration of whether the potential stress of COCs in discharging groundwater is likely to be discernible against this background. Evaluations should focus on receptor populations rather than individual receptors unless threatened or endangered species are affected.
     - ➢ The sensitivity of the receiving water ecosystem should be considered. A small, relatively pristine upland stream or an undisturbed wetland, for example, would be expected to be relatively sensitive ecosystems where the impacts of groundwater discharge may be significant. A historically industrialized river, or a river subjected to periodic dredging (such as for navigational purposes) is likely to have an altered and less sensitive ecosystem where the effects of groundwater discharge would be less significant.
     - ➢ Natural factors potentially affecting receptor species richness and diversity should be considered as well as the potential effects of discharging groundwater to understand the likely sources of any observed impacts. Numerous natural factors, many of which vary over time, have potentially significant impacts. These include the availability of prey species/food sources, sediment type (e.g. sandy vs. silty), turbidity, water temperature, oxygen content and other water chemistry factors, sediment dynamics and salinity.

4. Evaluate the potential for significant effects. Taking into account, information about the ability of the materials to accumulate in sediments or up the food chain and the sensitivity of the habitat, an evaluation can be made as to the potential for the material to have significant impacts. Biological effect concentrations in sediments may be estimated for non-polar organic chemicals and other divalent metals based on equilibrium partitioning theory and knowledge of the water-only effects concentrations for the chemicals of concern and concentrations of important binding phases in sediments (e.g., AVS-SEM, organic carbon).

5. Consider potential background sources of contaminant loading to surface water and sediments and their relative effects on sediment and environmental quality to help determine whether potential groundwater discharges are significant and can be differentiated from background effects. Potential sources of loading include:
   - Current upstream (and, in tidal waters, downstream) point source loadings such as NPDES discharges.
   - Current upstream (and, in tidal waters, downstream) non-point source loadings such as storm water runoff, combined sewer outfalls, agricultural runoff, atmospheric deposition, etc.
   - Historical use and impact to the surface water body (e.g. history of sediment contamination).

Evaluate whether existing information allows for an EI determination to be made (Step 6).

<u>"YE" – Yes, Migration of Contaminated Groundwater Under Control</u>

- If the preceding steps indicate that, based on weight of evidence, an ongoing, significant and adverse impact on the surface water or sediment ecology as a result of current groundwater discharge is unlikely (e.g. flux vs. receiving water flows indicate no impact or no constituents are COCs) then a "YE" determination can be made for this element of CA 750.
- If the information reviewed in the preceding steps indicates that the potential impacts of groundwater discharge on the surface water and sediment ecology cannot be differentiated from background, either

manmade (e.g. point source discharges, historical discharges) or natural (e.g. sediment type, temperature effects), a "YE" determination can be made, i.e.,

- If estimated SW concentrations resulting from GW discharge> screening levels but are <background and cannot be discerned from background contributions = YE

"IN" – More Information Needed

- If the information reviewed in the preceding steps indicates that the potential impacts of groundwater discharge on the surface water and sediment ecology are less than background but can be differentiated from background and are potentially significant, determine IN and collect additional data to assess specific effects, i.e.,
  - If estimated SW concentrations resulting from GW discharge ≥ screening levels but are < background and can be discerned from background contributions = IN, if potentially significant.

"NO" - Migration of Contaminated Groundwater is Not Under Control

- If, based upon this screening evaluation, the determination indicates that a significant ecological impact due to current groundwater discharge is likely (due to the nature of the receiving water, the discharge flux and the COCs discharged) and that this impact can likely be reasonably differentiated from background effects, then either an "IN" or a "NO" can be determined as appropriate based upon the potential significance of the problem. Additional site-specific data should be gathered to assess these particular effects.

Gather additional site-specific data to facilitate the EI determination

- If additional site-specific data are determined to be necessary, they should focus on the key outstanding questions remaining from the screening evaluation. It should be recognized that sediment chemistry and dynamics, groundwater discharge into surface water and surface water/sediment ecology are complex technical areas. Technical specialists should be consulted as appropriate.
  - Media sampling should focus on COCs and key physiochemical factors affecting contaminant partitioning (e.g. sediment grain size, organic carbon fraction, and, in cases involving metals, Acid-Volatile Sulfide- Simultaneously Extractable Metals (AVS-SEM) determinations).
  - Media sampling should be directed to groundwater discharge zones, and in general should include background or reference-area samples as well. Samples taken up and downstream of the discharge zone can be helpful in understanding the significance of the potential impact relative to areas where there is no known discharge.
  - Ecological evaluations should focus at the population level and on those receptors deemed important from an exposure or site-specific perspective, rather than individuals (unless threatened or endangered species are exposed), and should consider potential stressors of significance. Significant stressors are those which are known or suspected of impairing the reproductive capacity of the receptor or which bioaccumulate and subsequently are capable of entering important food chains.
  - Because of the inherent complexities of sampling and evaluating surface water and sediment data as it relates to groundwater discharge, it is extremely important that data quality objectives (DQO) are agreed upon by all parties prior to initiating sampling.

Evaluating additional site-specific media and ecological data

- Unlike for potential human health effects, there are relatively few numeric screening criteria available for ecological effects. These criteria need to be used carefully, as the range of variables in ecological systems is significant (as noted above). Many of the steps described above will be helpful tools for evaluating site-specific data and should be employed.
  - Sediment and surface water quality data should be evaluated against appropriate screening criteria relevant to the ecological setting, where available. These may be generic values (e.g. Ambient Water Quality Criteria) or site-specific (e.g. site-specific sediment screening criteria).
  - In addition to Federal and state criteria documents, the following may provide screening benchmarks.
    - *Toxicological Benchmarks for Screening of Potential Contaminants of Concern for Effects on Aquatic Biota on Oak Ridge Reservation: 1996 Revision*, Suter, GW II and CL Tsao, Oak Ridge National Laboratory, 1996)
    - *Toxicological Benchmarks for Screening Contaminants of Potential Concern for Effects on Sediment-Associated Biota: 1997 Revision*. Jones, D.S., G.W. Suter II, and R.N. Hull, Oak Ridge National Laboratory, Oak Ridge, TN, 1997.
    - Buchman, MF. 1999. NOAA Screening Quick Reference Tables, NOAA HAZMAT Report 99-1, Seattle WA, Coastal Protection and Restoration Division, National Oceanic and Atmospheric Administration, 12 pp.
    - Other relevant studies/databases
  - Where such screening suggests potential impacts an ecological evaluation should be performed to evaluate the specific impacts suggested by the screening.
  - If ecological impacts associated with discharging groundwater and discernible against background effects are determined to exist, their magnitude should be evaluated.

References/Resources

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Example Scenarios

The intent of the following scenarios is to illustrate the EI determination at Step 6, with varying amounts of data. If it is determined that sampling is required, the EPA and the regulated party should agree on specific sampling and data quality objectives. What does a "high hit" mean? How will data be evaluated? What are the Data Quality Objectives?

It should be noted that a YE determination (i.e., no current significant impact) does not preclude further remedial action. The YE determination only suggest that interim or final remedial response is not warranted in the "near-term".

Example 1: Potential release to a small stream

- Setting: Small intermittent stream with a gravel bed. Stream is not used for drinking water or recreational use.
- Release: Leaded gasoline in groundwater, ¼ mile from stream
- COCs:
  - BTEX levels in GW at 12 times the drinking water standard
  - Lead in GW below the Action level
- Surface Water Evaluation:
  - BTEX soluble but degradable, not bioaccumulative. Lead will sorb to soils and sediments. Materials unlikely to enter receiving water above criteria
- Sediment Evaluation:
  - Lead will potentially accumulate but it unlikely to get to stream and with no sediments lead is not issue
- EI Determination (weigh all evidence): "YE"
- Sampling Strategy: No sampling required

Remedial Response: None

Placeholder figure from USGS Circular 1139.
Groundwater and Surface Water A Single Resource (1999)

Example 2: Potential releases to a recreational lake

Placeholder figure from USGS Circular 1139.
Groundwater and Surface Water A Single Resource (1999)

- Setting: Lake used for recreational fishing, no background contamination
- Release:
  - Leaded gasoline in groundwater, wells on bank of stream
  - Also, Hg(/signature) in GW that has moved off-site
- COCs:
  - BTEX levels in GW at 12 times the drinking water standard
  - Lead in GW below the Action level
  - Hg greater than 20 times the eco-benchmarks in groundwater & detected in SW
- Surface Water Evaluation:
  - Based on tiered approach review, BTEX and lead not an issue
  - Hg still above the SW criteria after taking into account flow
- Sediment Evaluation:
  - BTEX and lead are not of concern
  - Hg may be present in sediment
- EI Determination (weigh all evidence): "IN", sampling advisable
- Sampling Strategy:
  - Develop Data Quality Objectives
  - Physical, hydrogeological characteristics,
  - Targeted sampling of SW to determine potential for impact to sediment.
  - Sediment sampling only if warranted necessary.

Remedial Response: To be determined

Example 3 Potential releases to a Large River with Significant Industrial Use

Placeholder figure from USGS Circular 1139. Groundwater and Surface Water A Single Resource (1999)

Setting:_Heavy use, tidally influenced, river that discharges to the ocean. Used as a major waterway. Industrial activity with permitted discharges since early 1900s of the same materials. Also, agricultural (primarily fruit orchards) as well as sewer discharges permitted along the length of river. Water used for process streams but not as a drinking water source.

Release: Groundwater contaminated as a result of long-term chemical manufacturing process over time. "Contaminated" groundwater has moved off-site. GW contains chlorinated solvents, arsenic, and a "signature" chemical. All materials are part of the manufacturing process and have NPDES permit limits.

COCs: As, TCE, VC

Surface Water Evaluation:

1. Compare available data to relevant criteria
2. Determine mass Flux
3. Estimate surface water concentration
4. Compare estimated concentration against relevant criteria; characterize potential significance
5. Compare to background; determine significance

Result of Surface Water Evaluation:

Groundwater discharge of organics <1% of NPDES mass discharge, organics volatile, arsenic background much higher than groundwater mass discharge

Sediment Evaluation :

1. Eco-toxicity, compare available data to available criteria
2. Determine propensity accumulate
3. Determine ecosystem sensitivity
4. Characterize potential significance
5. Compare to background; determine significance

Results of Sediment Evaluation:

Organic contamination does not sorb and is non-bioaccumulative, arsenic discharge could be problem, but well below background, and not discernable from background.

EI Determination (Weigh all the evidence): "YE"

Sampling Strategy: No sampling required

Summary of Factors Considered in Determining Groundwater to Surface Water Impacts Prior to Sampling

FACTOR	DESCRIPTION (WHAT IT IS) … .TO INCLUDE TYPICAL VALUES	IMPACT/IMPORTANCE (WHAT IT DOES) NOTES
GROUNDWATER PROPERTIES		
• Flux ($Q = kiA$)	The groundwater flux describes the groundwater discharge from the cross-sectional area of the plume into the stream Q (L^3/T). Q may be estimated as kiA where: k = hydraulic conductivity in (L/T); i = hydraulic gradient and A = cross sectional are of plume at point of stream intersection (L^2).	As flux increases, a greater amount of potentially contaminated water is expected to exit the site and enter the surface water.
• Concentration (C)	The concentration (mass/volume) of the COC in the groundwater determines the potential amount of COC entering the surface water from the groundwater source. Typically, an area-weighted average concentration provides a good estimate of potential impact from the groundwater leaving the site.	As concentration increases, the potential for impact increases. Use of maximum observed concentrations provides a worst case estimate whereas use of an "area-weighted" average provides a more realistic estimate of the mass of materials leaving the site in the groundwater.
SURFACE WATER (SW) PROPERTIES		
• Contaminant loading rate to surface water	The contaminant mass loading is determined from the groundwater flux and the concentration of COCs in the groundwater, i.e., Q x C.	Mass loading is important as it provides a measure of the mass of material entering the water body and whether this is a lot (potential significant impact) or a little.
• Surface water flow rate	The surface water flow effectively determines the volume of water that the contaminant mass will be diluted into. Typically, the low flow (e.g., 7Q10) is used for non-carcinogens and the harmonic mean is used for carcinogenic materials.	Use of a low flow condition ensures that the highest concentrations are determined. This is appropriate for evaluating potentially acute effects. However, since cancer effects are evaluated over a lifetime, mean flow conditions are more appropriate for carcinogens.
• Mixing zone	The mixing zone is that area where the groundwater discharges co-mingle with the surface water and is effectively diluted. Mixing zones are determined on a site-specific basis	Mixing zones are important because they represent the limit of the area of effective dilution beyond which is the area for comparison with "criteria".
• Tidal effects	Surface water tidal fluctuations have been shown to reduce concentrations in both the surface water body and in the tidally affected portions of a hydraulically connected aquifer due to natural flushing (Yim and Moshen, 1992)[1] . However, tidal action may cause COCs to enter the surface water system sooner, and may affect physicochemical processes that govern the environmental fate of a COC.	Tidal effects can reduce both groundwater and surface water concentrations through dilution. These effects need to be evaluated on a case-by-case basis.
• Effective dilution	Effective dilution is determined from diluting the mass load into surface water flow within the anticipated mixing zone. It provides an estimate of the surface water concentrations after the groundwater is combined. $C_{sw} = (Q_{gw} \times C_{gw})/Q_{sw}$	Effective dilution is a critical factor in these evaluations because this dilution determines the concentration that aquatic species will be exposed to.

1. Yim, Y. S. and M. F. N. Mohsen, 1992, "Simulation of Tidal Effects on Contaminant Transport in Porous Media", Ground Water, V 30 No. 1 Jan-Feb 1992.

Summary of Factors Considered in Determining Groundwater to Surface Water Impacts Prior to Sampling (cont)

SEDIMENT CHARACTERISTICS		
• Nature of the sediments	The nature of the sediments describes, for example, whether they are granular (sandy) or have a high organic carbon content. Granular sediments or sediments with f_{oc} of less than 0.2% (DiToro, 1991) are generally not considered to accumulate hydrophobic constituents (including metals). Clay content and cation exchange capacity (CEC) are important considerations for metals.	The nature of the sediments is an important factor in determining whether contaminants will sorb to the sediments or are released to the pore water, or whether the materials remain in the water column in the first place.
• Migration Potential	Sediment properties (i.e., organic carbon content, hydraulic conductivity, bulk density, and porosity), COC properties (K_{OC}), and site specific properties (sediment thickness and hydraulic gradient) should be used to calculate whether a COC may have penetrated the sediments and migrated into the bioavailable zone.	Calculation of sediment breakthrough time and comparison with the groundwater discharge history allows COCs that are unlikely to have penetrated the sediment to be screened out.
ECOSYSTEM/RECEPTOR CHARACTERISTICS		
• Use/Classification of the receiving water	Waters may be classified as potable, that is, they are used as a drinking water source or non-potable. The use/classification of the waters determines potential receptors and routes of exposure. For example, in non-potable waters, "limiting" exposures are more likely to be to aquatic receptors versus human ingestion as drinking water.	Realistic classification of the receiving water based on current use is one of the most important determinants of the appropriate/relevant water quality or sediment criteria for comparison.
• Receptor/Habitat sensitivity	The sensitivity of potential receptors/habitats varies based on site-specific conditions. For example, an intact wetland is more likely to have sensitive receptors than an industrialized or extensively developed river.	Defining actual receptors is another important determinant of appropriate and relevant water quality and sediment criteria.
• Other stressors	Other potential ecological stressors/factors unrelated to the groundwater discharge may have a significant impact relative to that from the discharge. Examples of stressors include: temperature, turbidity, oxygen levels, and seasonal conditions.	These other stressors play a role in putting the discharge in perspective.
OTHER SOURCES		
• Current and historical discharges	Other sources (current or historical) include, for example, past/current National Pollutant Discharge Elimination System (NPDES) discharges, storm water/combined sewer overflows and atmospheric deposition. These should be evaluated whether they come from the site or other sources. Past groundwater discharges should also be considered.	For purposes of the EI 750, understanding other potential sources to the surface water body could significantly aid in determining if current groundwater discharges can/or are impacting the system.

Summary of Factors Considered in Determining Groundwater to Surface Water Impacts Prior to Sampling (cont)

COC Properties		
• Aquatic and sediment toxicity	Aquatic and sediment criteria that relate COC toxicity to receptors have been developed by different organizations over time. It is important to select relevant criteria based on actual receptors and exposure routes. For potable waters, drinking water MCLs are appropriate but an MCL would not be appropriate if the receptors were aquatic organisms. Example sources of toxicity criteria that may be used for screening analysis are the EPA's Ambient Water Quality Criteria and Sediment Guidelines documents and the Oak Ridge National Laboratory Database.	Care should be taken that the conditions under which the criteria were developed are appropriate for the site conditions or at least are taken into account in the evaluation.

• Environmental fate characteristics	Important properties that determine environmental fate include the potential to volatilize, degrade and accumulate. These are described by:
	➢ Henry's constant (H) is an indication of the propensity of a chemical to volatilize from the aqueous state. If $H < 10^{-7}$ atm-m³/mol, COC will not volatilize rapidly. If $H > 10^{-3}$ atm-m³/mol, the COC will rapidly volatilize from the aqueous state.
	➢ Degradation characteristics including:
	    ➢ Biodegradation half-life. COCs with half-life values less that 1year are considered "biodegradable".
	    ➢ Hydrolysis half-life
	    ➢ Photo-degradation half-life. COCs must absorb at 290 nm or greater to photodegrade in surface waters.
	    ➢ Chemical oxidation/reduction. Chemical specific.
	➢ Accumulation potential (described below).
		The physical and chemical properties of a chemical determine its environmental fate, in effect, where the material will reside and in what concentrations. Volatilization and degradation processes remove the material from the water column and sediment and, so mitigate their potential effects.
		
		On the other hand, accumulation processes potentially enhance concentrations in the sediments or biota and may increase effects.

Summary of Factors Considered in Determining Groundwater to Surface Water Impacts Prior to Sampling (cont)

COC Properties (*cont*)		
• Sediment-water partitioning (accumulation potential in sediment)	The propensity for COCs to accumulate in sediments and to partition from sediments to sediment pore water can be described by partitioning coefficients, including its soil/water partition coefficient (K_d), organic carbon normalized partition coefficient, (K_{oc}) and its octanol-water partitioning coefficient (K_{ow}). ➢ For organics: $K_d = K_{oc} \times f_{oc}$. If $K_d > 10$, compound is generally considered immobile and will sorb to sediment. If $K_d < 1$, compound is generally considered to be mobile in water and will not tend to sorb to sediment. COCs with log 10 K_{oc} or log 10 K_{ow} less than 3 are generally not considered likely to accumulate in sediments. ➢ For inorganics: Di Toro *et al* (1991)[1] and others have proposed that sediment criteria based on an Equilibrium Partitioning (EqP) model are better predictors of toxicity rather than total metal concentration in the sediment (i.e., it is the metal concentration in the pore water rather than in the total metal in the sediment that is important). Formation of metal sulfides (that precipitate as a solid) has been found to be a dominant reaction in many sediments for several metals. Thus, this reaction removes metal from the pore water and so reduces the bioavailability (and toxicity) of the metal. Amorphous FeS is a source of the sulfide in many sediments and acid volatile sulfide (AVS) is a measure of the amorphous FeS present at a site. If the metal is simultaneously extracted (i.e., the metal extracted at the same time and in the same acid) is measured, and the concentration of the simultaneously extracted metal (SEM) is less than the AVS concentration, then the metal precipitates and is not bioavailable.	COCs that sorb strongly to sediments (and remain sorbed) are removed from the aqueous environment and their potential effects are mitigated. They are, in effect, not bioavailable. Thus, criteria based on an EqP model is favored over methods based on total metal concentration. The SEM-AVS approach is a very useful predictor of site-specific toxicity (based on available metal). However, since metal sulfides can oxidize, it is important to understand the metal species chemistry at the site.
• Bioaccumulation factor (accumulation potential up the food chain)	The bioaccumulation factors (BAF for water exposure and BSAF for sediment exposure) are the parameters that serve as a measure of COCs potential to accumulate up the food chain. The BAF is related to log K_{ow}. If COC log K_{ow} <3 or >6, the constituent is not considered to bioaccumulate.	The BAF and BSAF are important considerations because of the interest potential for effects at low aqueous or sediment concentration

1. Di Toro, D.M., Zarba, C. S. (1991). Technical Basis for the Equilibrium Partitioning Method for Establishing Sediment Quality Criteria. *Environ. Tox. Chem.* 11 (12): 1541 – 1548.

APPENDIX 4-1
ESTIMATION OF SEDIMENT BREAKTHROUGH

Estimation of Sediment Breakthrough

A simple estimation of breakthrough time for groundwater COC travelling through sediments can be developed from a one-dimensional advection calculation[1]. The pore velocity of groundwater (v) is calculated as usual using Darcy's Law:

$$v = \frac{Ki}{n}$$

where:
- K is the sediment hydraulic conductivity [L/T];
- i is the hydraulic gradient across the sediments [L/L]; and
- n is the porosity of the sediments [L^3/L^3].

The velocity of a COC (v^*) however, is retarded due to sorption processes within the sediments:

$$v^* = \frac{Ki}{n + \o_b \, f_{OC} \, K_{OC}}$$

where:
- $\o_b$ is the sediment bulk density [M/L^3];
- f_{OC} is the sediment organic carbon fraction [M/M]; and
- K_{OC} is the organic carbon partition coefficient of the COC [L^3/M].

Using the COC velocity, the time (t^*) required for a COC to break through sediments of thickness b, can be estimated by:

$$t^* = \frac{b\,(n + \o_b \, f_{OC} \, K_{OC})}{Ki}$$

Several of the parameters in this breakthrough time equation are properties of the sediment type. Assuming there are no site-specific data, these may be estimated through a visual characterization (i.e., muddy, sandy, gravelly) as indicated in Table 1 below.

[1] It should be noted that, for simplicity, this discussion neglects the processes of dispersion and diffusion within the sediments. These processes will cause a COC to break through earlier than the advective front that is calculated in this analysis. More sophisticated models for breakthrough time are available, but are probably unnecessary for this screening-level calculation.

Table 1. Typical Properties of Various Sediment Types[2]							
Parameter	Units	Gravel	Coarse Sand	Medium Sand	Fine Sand	Silt	Clay
Porosity (n)	%	30%	35%	40%	45%	50%	70%
Bulk Density (ρ_b)	kg/m^3	1.5	1.2	1	0.9	0.8	0.6
OC Fraction (f_{OC})	%	0.01%	0.10%	1%	2%	5%	10%
Hydraulic Conductivity (K)	m/d	250	5	2	0.5	0.01	0.0001

Site specific parameters in the breakthrough time equation presented above include the hydraulic gradient and sediment thickness, while K_{OC} is a COC-specific property. Therefore, with knowledge of the type and thickness of sediment and the hydraulic gradient at the site, an estimate of the breakthrough time for a given COC can be estimated from a chart similar to that shown in Figure 2, which represents calculated values of t^* for various combinations of these parameters.

The expected breakthrough time can then be compared to the time at which the plume is expected to have reached the surface water body, and an assessment of whether the COC has penetrated the sediments can be made. Consider an example site in which a plume may have been actively discharging to a stream for a decade. As shown by Figure 2, if a meter of sediment is present, penetration of the sediments may have occurred for COCs having a log K_{OC} less than 6, unless the sediments consist of silty material, in which breakthrough may only have occurred for low K_{OC} compounds and high hydraulic gradients.

2 Values in this table are based on ranges given in Domenico and Schwartz (1990) and Van Rijn (1993).

Figure 2. Breakthrough Time Estimation for a Range of Sediment Types and Hydraulic Gradient Values